Modelling of catalytic reactors with catalyst deactivation
I. Pseudo-homogeneous model of a plug-flow reactor

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The paper deals with modelling of catalytic reactors in which an irreversible catalyst deactivation takes place. The dimensionless model equations are derived for the pseudo-homogeneous model of a plug-flow reactor, an algorithm for their solution is proposed. The obtained results are compared with experimental ones in the case of hydrogenation of benzene on a nickel catalyst with thiophene as the poison.

Работа посвящена моделированию каталитических реакторов, в которых происходит необратимая дезактивация катализатора. Приводится вывод модельных уравнений в безразмерном виде для псевдогомогенной модели реактора с поршневым потоком, алгорифм решения указанных уравнений и сравнение полученных результатов с экспериментом. Указаны результаты для модельной системы: гидрогенирование бензола на никелевом катализаторе, каталитический яд — тиофен.

The deactivation of industrial catalysts is of considerable practical interest. It leads to a decrease of the performance of the catalytic reactor which requires the regeneration or replacement of the catalyst in certain intervals. That means a stand-still of the reactor and results in production loss and increase of running costs. In some industrial processes consumption of catalyst is the most important component of the running costs.

Although the phenomenon of deactivation has been known for a long time, many of its aspects are not satisfactorily understood. According to today understanding there are three basic mechanisms of deactivation:

a) Poisoning — occupancy of catalytic active sites as a result of strong chemisorption of some component of the reaction mixture; depending on whether the chemisorption is reversible or irreversible, the poisoning also can be reversible or irreversible.

b) Fouling — decomposition of reactants or products on the surface of the catalyst with depositing of high-molecular substances, or even, solid carbon.

c) Aging — loss of activity caused by sintering or recrystallization of the active component.

A detailed review of the problem of deactivation has been published by *Butt* [1]. Among recent papers [2, 3] should be mentioned, involving a detailed treatment of the modelling of a tubular catalytic reactor with catalyst deactivation using simple model equations of the reaction and deactivation kinetics. The activity profiles in a reactor for various models of catalyst poisoning have been published by *Mikuš et al.* [4]. Further, a large number of papers have been published dealing with the process of catalyst poisoning in various particular systems. These papers are, however, oriented experimentally rather than on the modelling itself.

Our aim is to develop a model of a catalytic reactor with catalyst deactivation on various levels of complexity, in the dimensionless form and to work out effective numerical algorithms for its solution. In this paper, the most simple model of a plug-flow reactor with perfect heat exchange between catalyst and gas is discussed.

Description of the kinetics of a catalytic reaction including catalyst poisoning

During the reaction on a catalyst which undergoes a gradual deactivation, the reaction rate is decreasing with time under otherwise constant conditions (temperature, composition, and flow rate of the reaction mixture). The instantaneous reaction rate depends not only on the composition of the reaction mixture and the temperature but also on the amount of poison adsorbed

$$\dot{\xi}_{\mathrm{W}} = \dot{\xi}_{\mathrm{W}}(C_i, T, a_{\mathrm{T}}) \tag{1}$$

In most cases, if the mechanism of the deactivation is of chemical nature, the right side of eqn (*1*) can be expressed as a product of two terms. The first term expresses the reaction rate on the fresh catalyst, the second one expresses the decrease of activity caused by the poisoning

$$\dot{\xi}_{\mathrm{W}}(C_i, T, a_{\mathrm{T}}) = \dot{\xi}^{*}_{\mathrm{W}}(C_i, T) \cdot \Phi(a_{\mathrm{T}}) \tag{2}$$

$$0 \leqslant \Phi \leqslant 1$$

Eqn (*2*) is to be completed by the rate equation of the poison chemisorption

$$\frac{\mathrm{d}a_\mathrm{T}}{\mathrm{d}t} = \mathrm{f}(C_i, T, a_\mathrm{T}) \tag{3}$$

and by the relation between the relative activity and the amount of the poison adsorbed

$$\Phi = \Phi(a_\mathrm{T}) \tag{4}$$

The kinetics of the catalytic reaction itself can be described by empirical or Langmuir—Hinshelwood kinetic equations. Analogously, also the rate of the adsorption of the poison can be described using various empirical or model equations. A variety of equations are being used to express the dependence of the relative activity on the amount of the poison adsorbed; *e.g.* for the so-called nonselective poisoning the linear equation

$$\Phi = 1 - \alpha_1 a_\mathrm{T} \tag{5}$$

and for the so-called selective poisoning equations like [1, 5]

$$\begin{gathered} \Phi = \exp(-\alpha_2 a_\mathrm{T}) \\ \frac{1}{\Phi} = 1 + \alpha_3 a_\mathrm{T} \\ \Phi = (\alpha_4 a_\mathrm{T})^\gamma \end{gathered} \tag{6}$$

Pseudo-homogeneous model of a plug-flow reactor with perfect heat exchange between catalyst and gas

As a first approximation to the description of the catalyst deactivation in a fixed-bed reactor, the simplest pseudo-homogeneous model with plug-flow has been chosen. In this model the catalyst bed is treated as a homogeneous medium with plug-flow of the gas phase [6, 7].

Assuming that in the reactor only one catalytic reaction and only one deactivation process takes place, the model consists of the following equations:

— mass balance of the key component

$$\varepsilon \frac{\partial C_\mathrm{B}}{\partial t} + w \frac{\partial C_\mathrm{B}}{\partial z} + \varrho_\mathrm{b} \dot{\xi}_\mathrm{W} = 0 \tag{7}$$

— mass balance of the poison

$$\varepsilon \frac{\partial C_\mathrm{T}}{\partial t} + \varrho_\mathrm{b} \frac{\partial a_\mathrm{T}}{\partial t} + w \frac{\partial C_\mathrm{T}}{\partial z} = 0 \tag{8}$$

— enthalpy balance

$$-(\varrho_b c_{ps} + \varepsilon \varrho_g c_{pg}) \frac{\partial T}{\partial t} - w \varrho_g c_{pg} \frac{\partial T}{\partial z} + (-\Delta H) \varrho_b \dot{\xi}_W =$$

$$= \frac{4h}{\mathrm{d_t}} (\mathrm{T} - \mathrm{T_c}) \qquad (9)$$

— kinetic equation of the catalytic reaction (*1*) and

— rate equation of the poison chemisorption (*3*).

The boundary conditions for the reactor inlet are

$$z = 0, \qquad t > 0; \qquad \begin{aligned} C_B &= C_{B0} = \text{const} \\ C_T &= C_{T0} = \text{const} \\ T &= T_0 \;\, = \text{const} \end{aligned} \qquad (10)$$

The initial conditions express the presumption that the poison was started to be introduced at time $t = 0$, *i.e.* at $t = 0$ no poison was in the bed and the profiles of the concentrations and the temperature were those of the steady state of the reactor with fresh catalyst, *i.e.*

$$t = 0, \qquad z \geqslant 0; \qquad a_T = 0$$

$$w \frac{\mathrm{d}C_B}{\mathrm{d}z} + \varrho_b \dot{\xi}_W^* = 0 \qquad (11)$$

$$w \varrho_g c_{pg} \frac{\mathrm{d}T}{\mathrm{d}z} + (-\Delta H)\, \varrho_b \dot{\xi}_W^* = \frac{4h}{d_t} (T - T_c)$$

The system of eqns (*7—9*) with the boundary and initial conditions (*10*) and (*11*) is valid under following assumptions:

a) The density of the reaction mixture is constant.

b) The amount of the key component adsorbed on the active sites of the catalyst is negligible.

c) The heat exchange between catalyst and gas is perfect, so the temperature of both of them is the same.

d) The heat released by the chemisorption of the poison is negligible.

After introducing dimensionless variables

$$Z = \varrho_b \xi_W^0 z / (C_{B0} w) \qquad A_T = a_T / a_{T0}^*$$

$$\tau = t / t^0 \qquad \dot{\Xi} = \dot{\xi}_W / \dot{\xi}_W^0$$

$$Y_B = C_B / C_{B0} \qquad \Theta = \frac{(T - T_0) \varrho_g c_{pg}}{(-\Delta H) C_{B0}} \qquad (12)$$

$$Y_T = C_T / C_{T0} \qquad \Theta_c = \frac{(T_c - T_0) \varrho_g c_{pg}}{(-\Delta H) C_{B0}}$$

and parameters

$$\delta = \frac{\varepsilon C_{\mathrm{B0}}}{\varrho_{\mathrm{b}} \dot{\xi}_{\mathrm{w}}^{0} t^{0}} \qquad G = \frac{C_{\mathrm{B0}} a_{\mathrm{T0}}^{*}}{\dot{\xi}_{\mathrm{w}}^{0} t^{0} C_{\mathrm{T0}}}$$

$$R_{\mathrm{s}} = \frac{(\varrho_{\mathrm{b}} c_{\mathrm{ps}} + \varepsilon \varrho_{\mathrm{g}} c_{\mathrm{pg}}) C_{\mathrm{B0}}}{\varrho_{\mathrm{g}} c_{\mathrm{pg}} \varrho_{\mathrm{b}} \dot{\xi}_{\mathrm{w}}^{0} t^{0}} \qquad F = \frac{4 h C_{\mathrm{B0}}}{d_{\mathrm{t}} \varrho_{\mathrm{b}} \dot{\xi}_{\mathrm{w}}^{0} \varrho_{\mathrm{g}} c_{\mathrm{pg}}} \tag{13}$$

the balances (*7—9*) become dimensionless

$$\delta \frac{\partial Y_{\mathrm{B}}}{\partial \tau} + \frac{\partial Y_{\mathrm{B}}}{\partial Z} + \dot{\Xi} = 0 \tag{14}$$

$$\delta \frac{\partial Y_{\mathrm{T}}}{\partial \tau} + G \frac{\partial A_{\mathrm{T}}}{\partial \tau} + \frac{\partial Y_{\mathrm{T}}}{\partial Z} = 0 \tag{15}$$

$$R_{\mathrm{s}} \frac{\partial \Theta}{\partial \tau} + \frac{\partial \Theta}{\partial Z} = \dot{\Xi} - F(\Theta - \Theta_{\mathrm{c}}) \tag{16}$$

The rate equations of the catalytic reaction and the chemisorption of the poison are

$$\dot{\Xi} = \dot{\Xi}(Y_{\mathrm{i}}, \Theta, A_{\mathrm{T}}) \tag{17}$$

$$\mathrm{d}A_{\mathrm{T}}/\mathrm{d}\tau = \varphi(Y_{i}, \Theta, A_{\mathrm{T}}) \tag{18}$$

respectively. The boundary and initial conditions (*10*) and (*11*) transform in

$$\begin{array}{lll} Z = 0, \quad \tau > 0; & Y_{\mathrm{B}} = Y_{\mathrm{T}} = 1, \quad \Theta = 0 & (19) \\ \tau = 0, \quad Z \geqslant 0; & A_{\mathrm{T}} = 0 & \\ & \mathrm{d}Y_{\mathrm{B}}/\mathrm{d}Z = -\dot{\Xi}^{*} & (20) \\ & \mathrm{d}\Theta/\mathrm{d}Z = \dot{\Xi}^{*} - F(\Theta - \Theta_{\mathrm{c}}) & \end{array}$$

In the relations (*12*) and (*13*), $\dot{\xi}_{\mathrm{w}}^{0} = \dot{\xi}_{\mathrm{w}}^{*}(C_{i0}, T_{0})$ is the reaction rate on the fresh catalyst corresponding to the composition and the temperature of the feed. Its concrete form depends on the kinetic equation used, as it will be illustrated further in this paper. Since it is deactivation which is responsible for the time dependence of the reaction rate, the time t^{0} is the characteristic deactivation time the concrete expression of which again depends on the rate equation for deactivation.

The expressions for the dimensionless parameters (*13*) are rather cumbersome and unusual. This is because the dimensionless space coordinate Z is defined by using the rate of catalytic reaction, while the dimensionless time τ is defined by the rate of deactivation. However, such a choice is justified in our case, since the temperature and concentration profiles in the reactor, *i.e.* the spatial distribution of the concentrations and the temperature, are determined primarily by the catalytic reaction, while the change of these profiles with time is determined by the rate of the deactivation of the catalyst.

Mathematical description of the catalytic hydrogenation of benzene with thiophene as the poison

The mathematical model has been developed using the rate equation of the form

$$\dot{\xi}_W = \Phi \, \frac{k_\infty K_\infty C_B C_H \exp\left[-(Q+E)/RT\right]}{1 + K_\infty C_B \exp\left(-Q/RT\right)} \tag{21}$$

The reasons for the choice of this equation are explained in Experimental. From eqn (*21*) follows the definition of $\dot{\xi}_W^0$

$$\dot{\xi}_W^0 = \frac{k_\infty K_\infty C_{B0} C_{H0} \exp\left[-(Q+E)/RT_0\right]}{1 + K_\infty C_{B0} \exp\left(-Q/RT_0\right)} \tag{22}$$

Thus the expression for the dimensionless reaction rate is

$$\dot{\Xi} = \Phi \, \frac{(1+\varkappa_B) Y_B Y_H \exp\left[(\alpha_i + \alpha_k)\beta\Theta/(1+\beta\Theta)\right]}{1 + \varkappa_B Y_B \exp\left[\alpha_k \beta\Theta/(1+\beta\Theta)\right]} \tag{23}$$

where

$$\begin{gathered} \varkappa_B = K_0 C_{B0} = K_\infty C_{B0} \exp\left(-Q/RT_0\right) \\ \alpha_i = E/(RT_0) \\ \alpha_k = Q/(RT_0) \\ \beta = \frac{(-\Delta H) C_{B0}}{\varrho_g c_{pg} T_0} \end{gathered} \tag{24}$$

To describe the deactivation rate, the following relation has been chosen

$$\mathrm{d}\Phi/\mathrm{d}t = -k_{T\infty} \Phi C_T \exp\left(-E_T/RT\right) \tag{25}$$

Let us prove that this equation corresponds to the following idea of the poisoning mechanism: the poisoning takes place as a consequence of the irreversible thiophene adsorption on the active sites resulting in their gradual occupancy for the catalytic reaction. The adsorption rate of the poison is equal on all nonoccupied sites regardless of whether they are free or whether benzene, cyclohexane or the intermediates of the hydrogenation reaction are adsorbed on them, and it can be expressed by a Langmuir-type rate equation

$$\mathrm{d}a_T/\mathrm{d}t = k_{T\infty} C_T (a_L - a_T) \exp\left(-E_T/RT\right) \tag{26}$$

The fractional activity of the catalyst equals the ratio of concentration of the active sites not yet occupied by the thiophene to their total concentration

$$\Phi = 1 - a_T/a_L \tag{27}$$

After expressing a_T from eqn (*27*) and substituting it into eqn (*26*) and rearranging, the relation (*25*) is obtained.

From eqn (*26*) it follows that at any temperature and thiophene concentration in the feed it holds

$$a_{T0}^{*} = a_L \tag{28}$$

hence

$$A_T = a_T/a_L = 1 - \Phi \tag{29}$$

and the balance (*15*) becomes

$$\delta \frac{\partial Y_T}{\partial \tau} - G \frac{\partial \Phi}{\partial \tau} + \frac{\partial Y_T}{\partial Z} = 0 \tag{30}$$

The characteristic time t^0 has been chosen in order to satisfy the condition

$$k_{T0} C_{T0} t^0 = 1 \tag{31}$$

where

$$k_{T0} = k_{T\infty} \exp\left(-E_T/RT_0\right) \tag{32}$$

is the rate constant of the adsorption of thiophene at the temperature T_0. Then the rate of deactivation transforms into the dimensionless form

$$\dot{\Phi} = \partial \Phi/\partial \tau = -\Phi Y_T \exp\left(\alpha_T \beta \Theta/(1+\beta\Theta)\right) \tag{33}$$

where

$$\alpha_T = E_T/RT_0 \tag{34}$$

The quasi-steady state approximation

If the deactivation rate is much lower than the rate of the catalytic reaction, the parameters δ and R_s are very small, so that the corresponding terms in the balance equations are negligible. So eqns (*14—16*) become

$$\partial Y_B/\partial Z = -\dot{\Xi} \tag{35}$$

$$\partial Y_T/\partial Z = G(\partial \Phi/\partial \tau) \tag{36}$$

$$\partial \Theta/\partial Z = \dot{\Xi} - F(\Theta - \Theta_c) \tag{37}$$

The isothermal reaction

In case of isothermal reaction $T = T_0$, thus $\Theta = 0$ and the dimensionless catalytic reaction rate equation (*23*) transforms to

$$\dot{\Xi} = \Phi \frac{(1+\varkappa_{\mathrm{B}})Y_{\mathrm{H}}Y_{\mathrm{B}}}{1+\varkappa_{\mathrm{B}}Y_{\mathrm{B}}} \tag{38}$$

and the deactivation rate equation (*25*) becomes

$$\mathrm{d}\Phi/\mathrm{d}t = -k_{\mathrm{T0}}C_{\mathrm{T}}\Phi \tag{39}$$

or in the dimensionless form

$$\mathrm{d}\Phi/\mathrm{d}\tau = \dot{\Phi} = -\Phi Y_{\mathrm{T}} \tag{40}$$

It can be seen from eqns (*39*) and (*40*) that under isothermal conditions and under the above assumptions on the deactivation mechanism, the latter is independent of the catalytic reaction. Formally, this reflects in the fact that eqns (*39*) and (*40*) do not involve any variable relating to the chemical reaction. In such a case the deactivation process can be described independently of the catalytic reaction, formally in the same way as the adsorption in a fixed bed with the favourable form of the adsorption isotherm. As it is known, in this case after certain time the so-called "constant-pattern conditions" will take place and the adsorption zone without changing the concentration profile moves down the bed with constant velocity [8]

$$v = \frac{wC_{\mathrm{T0}}}{(\varepsilon C_{\mathrm{T0}} + \varrho_{\mathrm{b}}a^{*}_{\mathrm{T0}})} \tag{41}$$

Analogously, in the case of a catalytic reaction with catalyst deactivation a steady "deactivation wave" will move along the reactor in which the concentration profiles of benzene and thiophene will not change.

After introducing the transformed time variable

$$u = t - z/v \tag{42}$$

and in the dimensionless form

$$U = \tau - (B+\delta)Z \tag{43}$$

the mass balances (*14*) and (*15*) for the steady movement of the deactivation wave transform to ordinary differential equations

$$\mathrm{d}Y_{\mathrm{B}}/\mathrm{d}U = (1/G)\dot{\Xi} \tag{44}$$

$$\mathrm{d}A_{\mathrm{T}}/\mathrm{d}U = \mathrm{d}Y_{\mathrm{T}}/\mathrm{d}U \tag{45}$$

with boundary conditions

$$U = -\infty: \qquad Y_{\mathrm{B}} = Y_{\mathrm{T}} = A_{\mathrm{T}} = 0 \tag{46}$$

$$U = +\infty: \qquad Y_{\mathrm{B}} = Y_{\mathrm{T}} = A_{\mathrm{T}} = 1 \tag{47}$$

From the relations (*29*), (*40*), and (*45*) it is possible to derive the equations for the steady deactivation wave

$$Y_{\mathrm{T}}=1-\Phi \tag{48}$$

$$\mathrm{d}\Phi/\mathrm{d}U=\dot{\Phi}=-\Phi(1-\Phi) \tag{49}$$

$$\mathrm{d}Y_{\mathrm{T}}/\mathrm{d}U=Y_{\mathrm{T}}(1-Y_{\mathrm{T}}) \tag{50}$$

and after integration

$$\Phi=1/(1+\exp(U)) \tag{51}$$

$$Y_{\mathrm{T}}=\exp(U)/(1+\exp(U)) \tag{52}$$

After dividing eqn (*44*) by eqn (*50*) and substituting for $\dot{\Xi}$ from eqn (*38*), a differential equation relating Y_{B} and Y_{T} is obtained

$$\frac{\mathrm{d}Y_{\mathrm{B}}}{\mathrm{d}Y_{\mathrm{T}}}=\frac{(1+\varkappa_{\mathrm{B}})Y_{\mathrm{B}}Y_{\mathrm{H}}}{B(1+\varkappa_{\mathrm{B}}Y_{\mathrm{B}})Y_{\mathrm{T}}} \tag{53}$$

If the hydrogenation takes place in a large excess of hydrogen, its concentration throughout the entire bed is practically constant and $Y_{\mathrm{H}}\approx 1$. Then the integration of eqn (*53*) gives a relation between the benzene and thiophene concentrations in the steady deactivation wave

$$\ln Y_{\mathrm{T}}=\frac{B}{1+\varkappa_{\mathrm{B}}}[\ln Y_{\mathrm{B}}-\varkappa_{\mathrm{B}}(1-Y_{\mathrm{B}})] \tag{54}$$

and finally the substitution for Y_{T} from eqn (*52*) yields an implicit equation for the concentration profile of benzene in the steady wave

$$U-\ln(1-\exp(U))=\frac{B}{1+\varkappa_{\mathrm{B}}}[\ln Y_{\mathrm{B}}-\varkappa_{\mathrm{B}}(1-Y_{\mathrm{B}})] \tag{55}$$

Numerical solution of the model equations

In this paper the algorithm of the solution of the model dimensionless equations for the quasi-steady state is proposed. Those are eqns (*35*), (*36*), (*38*), and (*40*) for the isothermal case (Model 1) and eqns (*35*), (*36*), (*37*), (*23*), and (*33*) for the nonisothermal one (Model 2).

Unlike the equations describing the rate of the deactivation, which contains also the time derivative, the benzene and thiophene mass balances and the enthalpy balance (in the case of Model 2) contain only space derivatives. This is why predictor—corrector method has been employed for the solution of the system of governing equations. In the mass and enthalpy balances prediction along the reactor and in the deactivation rate equation in the time has been made.

The relations for computing the values of predictor are

$$\hat{Y}_{\mathrm{B}}(I) = Y_{\mathrm{B}}(I-1,J+1) - \Delta Z\dot{\Xi}(I-1,J+1) \tag{56}$$

$$\hat{Y}_{\mathrm{T}}(I) = Y_{\mathrm{T}}(I-1,J+1) + \Delta ZG\dot{\Phi}(I-1,J+1) \tag{57}$$

$$\begin{aligned}\hat{\Theta}(I) = \Theta(I-1,J+1) + \Delta Z\{\dot{\Xi}(I-1,J+1) - \\ - F[\Theta(I-1,J+1) - \Theta_{\mathrm{c}}]\}\end{aligned} \tag{58}$$

$$\hat{\Phi}(I) = \Phi(I,J) + \Delta\tau\dot{\Phi}(I,J) \tag{59}$$

where I and J are space and time index, respectively. The nonlinear terms as the reaction and deactivation rate are at the $I-1$ space step (in eqns (*56—58*)) and $J-1$ time step (in eqn (*59*)), respectively.

The corrector equations are

$$Y_{\mathrm{B}}(I,J+1) = Y_{\mathrm{B}}(I-1,J+1) - \Delta Z\dot{\Xi}\left(I-\frac{1}{2},\, J+1\right) \tag{60}$$

$$Y_{\mathrm{T}}(I,J+1) = Y_{\mathrm{T}}(I-1,J+1) + \Delta ZG\dot{\Phi}\left(I-\frac{1}{2},J+1\right) \tag{61}$$

$$\begin{aligned}\Theta(I,J+1) = \Theta(I-1,J+1) + \Delta Z\Big[\dot{\Xi}\left(I-\frac{1}{2},J+1\right) - \\ - F(\bar{\Theta} - \Theta_{\mathrm{c}})\Big]^2\end{aligned} \tag{62}$$

$$\Phi(I,J+1) = \Phi(I,J) + \Delta\tau\dot{\Phi}\left(I,J+\frac{1}{2}\right) \tag{63}$$

In eqns (*60—62*) the nonlinear terms are computed from the values

$$\bar{Y}_{\mathrm{B}} = \frac{Y_{\mathrm{B}}(I-1,J+1) + \hat{Y}_{\mathrm{B}}(I)}{2}$$

$$\bar{Y}_{\mathrm{T}} = \frac{Y_{\mathrm{T}}(I-1,J+1) + \hat{Y}_{\mathrm{T}}(I)}{2}$$

$$\bar{\Theta} = \frac{\Theta(I-1,J+1) - \hat{\Theta}(I)}{2}$$

$$\bar{\Phi} = \frac{\Phi(I-1,J+1) + \hat{\Phi}(I)}{2}$$

and in eqn (*63*) the rate $\dot{\Phi}$ from the values

$$\bar{\Phi} = \frac{\Phi(I,J) + \hat{\Phi}(I)}{2}, \qquad \bar{Y}_{\mathrm{T}} = \frac{Y_{\mathrm{T}}(I,J) + Y_{\mathrm{T}}(I,J+1)}{2}$$

$$\bar{\Theta} = \frac{\Theta(I,J) + \Theta(I,J+1)}{2}$$

The boundary conditions are given by eqns (*19*). The initial conditions are given by the solution of the steady state equations at unit activity. For the isothermal Model 1 this solution can be expressed in the closed form (for $Y_H \approx 1$)

$$Z = \frac{1}{1 + \varkappa_B} [\varkappa_B(1 - Y_B) \ln Y_B] \tag{64}$$

$$Y_T = \exp(-GZ) \tag{65}$$

Since the values of Y_B for particular Z's are needed in further computations, eqn (*64*) has been solved numerically, by a similar scheme as in the quasi-steady state.

Experimental

To check the adequacy of the described models two series of experiments have been performed:

A. In an isothermal rotating basket reactor, to measure the kinetics of the benzene hydrogenation and of the poisoning reaction under the experimental conditions of interest.

B. In a tubular reactor, to compare computed concentrations and temperature profiles with experimental ones.

We have chosen benzene hydrogenation on Ni catalyst as a model reaction system (an exothermic and at low temperature irreversible reaction) and thiophene as a catalyst poison.

A. Reaction kinetics and catalyst deactivation rate measurements

The experiment has been carried out in an isothermal rotating basket reactor. The reactor is described in [9]. The high revolution of the stirrer enabled us to assume perfect mixing and to neglect external diffusion. The volume of the gaseous phase in the reactor was approximately 100 ml. The temperature in the reactor was regulated with accuracy 0.4 %. The composition of the outflowing stream was measured during the experiment by the gas chromatograph.

To measure kinetics of the reaction, pure benzene was fed into the reactor (steady state measurement). To examine catalyst deactivation, the inlet has been switched to a thiophene-containing feed. In such a way time dependence of the concentration of substances present has been followed up to the total catalyst deactivation. The reaction and poisoning kinetics have been measured at six temperatures in the range from 60 to 150 °C and at several inlet benzene and thiophene concentrations [10].

To describe the rate of benzene hydrogenation we tested several reaction rate equations [2, 11]. The best fit for the given system and experimental conditions is given by the equations

$$\dot{\xi}_W = \frac{kKC_BC_H}{(1+KC_B)^2} \tag{66}$$

$$\dot{\xi}_W = \frac{kKC_BC_H}{1+KC_B} \tag{67}$$

in which $k = k_\infty \exp(-E/RT)$ and $K = K_\infty \exp(-Q/RT)$. To model the tubular reactor the more simple relation (*67*) has been chosen and the parameters k_∞, K_∞, E, and Q have been computed using the least-square estimation method. As the minimized function we have chosen

$$\mathcal{F} = \sum_{i=1}^{n} \sum_{j=1}^{m} [(\dot{\xi}_{W_{ij}})_{\text{exp}} - (\dot{\xi}_{W_{ij}})_{\text{calc}}]^2 \tag{68}$$

where n is the number of isothermal experiments and m the number of measurements at a given temperature. The value of $(\dot{\xi}_{W_{ij}})_{\text{exp}}$ has been computed from the experimental values by the mass balance of continuous stirred tank reactor [10].

$$\dot{\xi}_W = \frac{\dot{V}_0C_{B0}X_B}{W} \tag{69}$$

Eqn (*25*) has been chosen as the deactivation rate equation in which we do not consider the temperature dependence of the constant k_T, since in our experiments the temperature influence on the deactivation process was not significant. Eqn (*25*) then has the form

$$\mathrm{d}\Phi/\mathrm{d}t = -k_T\Phi C_T \tag{70}$$

The catalyst activity Φ has been computed from the benzene balance and reaction rate equation (*21*). The benzene balance in the continuous stirred tank reactor may be written in the form

$$\dot{\xi}_W = \frac{1}{W}\left[\dot{V}_0(C_{B0}-C_B) - V\frac{\mathrm{d}C_B}{\mathrm{d}t}\right] \tag{71}$$

The value of the catalyst deactivation rate $\dot{\Phi}$ has been computed numerically. The value of the constant k_T has been estimated by the least-square method.

The numerical values of kinetic rate equations parameters obtained from the rotating basket reactor measurements are: $k_\infty = 0.0215\ \text{m}^3\ \text{kg}^{-1}\ \text{s}^{-1}$; $K_\infty = 116.04\ \text{m}^3\ \text{mol}^{-1}$; $E = 1.714\ \text{kJ mol}^{-1}$; $Q = 34.24\ \text{kJ mol}^{-1}$; $k_{T\infty} = 0.703 \times 10^{-2}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}$.

B. Deactivation process measurements in the tubular fixed bed reactor

The scheme of the laboratory tubular reactor is in Fig. 1. The characteristics of the reactor are: reactor length 0.8 m; reactor internal diameter 0.016 m; thermowell external diameter 4.8 mm. The temperature profile has been measured by a movable thermocouple placed in an axial thermowell. The reactor was heated by silicon oil, flowing through the external tube. Its volumetric flow rate has been kept sufficiently high in order to secure equality of the inlet and exit temperatures. The catalyst bed was placed between the glass beads of the same mesh size as the catalyst. In this way the reaction gas entered onto the catalyst bed by a steady flow rate, preheated to the reaction temperature. The composition of the exit gas has been analyzed by a gas chromatograph.

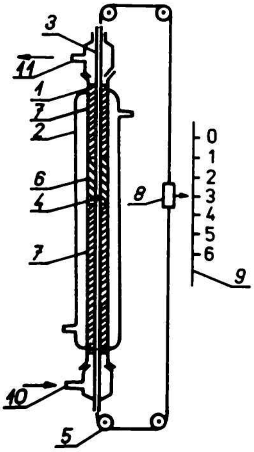


Fig. 1. Laboratory tubular reactor.
1. Internal tube
2. external tube
3. thermowell
4. thermocouple
5. pulley
6. catalyst bed
7. glass beads
8. thermocouple axial position indicator
9. scale
10. inlet of reacting gas
11. gas exit

The temperature measured at the axis of the reactor has been averaged under the assumption of parabolic radial temperature profile [12].

Results and discussion

The results of this paper correspond to the operating conditions: catalyst bed length 0.11 m; catalyst mass 11.486 g; inlet benzene concentration 2.071 mol m^{-3}; inlet thiophene concentration 3.81×10^{-2} mol m^{-3}; volumetric flow rate 1.015 ml s^{-1}; inlet temperature 71.6 °C; catalyst diameter 1.2—1.6 mm, and to the values of the dimensionless parameters computed from the reaction kinetics, reactor characteristics, and characteristics of a given measurement:

$\varkappa_B = 0.00156$; $\alpha_i = 0.598$; $\alpha_k = 11.95$; $\beta = 0.872$; $Z_L = 4.683$; $\Theta_c = 0.005$. The values of parameters G and F we could not estimate a priori from the above data (we do not know the characteristic time of the deactivation process and overall heat transfer coefficient). Rather, we have estimated them a posteriori so that the best fit of the model and the experimental concentration and temperature dependences has been obtained.

Figs. 2 and 3 illustrate experimental concentrations *vs.* time dependences together with the computed ones for the isothermal Model 1 and for several values of the parameter G. With increasing value of this parameter the slope of both the curves becomes steeper.

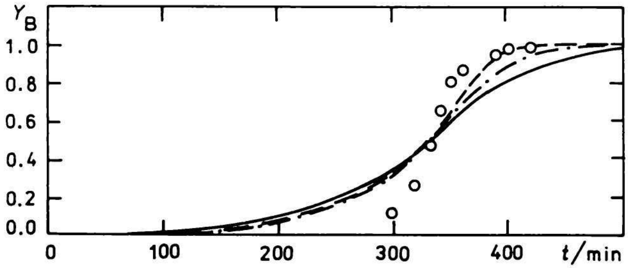


Fig. 2. Dimensionless benzene concentration *vs.* time.
○ Experiment; Model 1:
—— $G = 2$; —·—· $G = 4$; — — — $G = 10$.

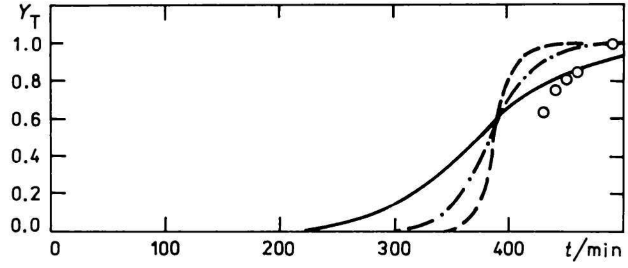


Fig. 3. Dimensionless thiophene concentration *vs.* time.
○ Experiment; Model 1:
—— $G = 2$; —·—· $G = 4$; — — — $G = 10$.

In Figs. 4 and 5 these experimental dependences are compared with those computed for the nonisothermal Model 2 with values $G = 15$ and $F = 34$. The transient concentration profiles in the bed are shown in Figs. 6 and 7. The transient

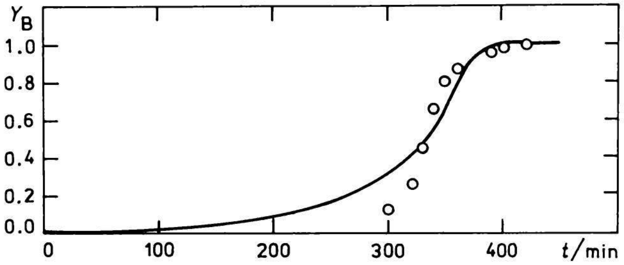


Fig. 4. Dimensionless benzene concentration *vs.* time.
○ Experiment; ——— Model 2.

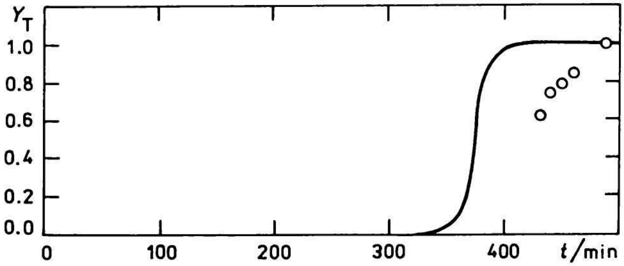
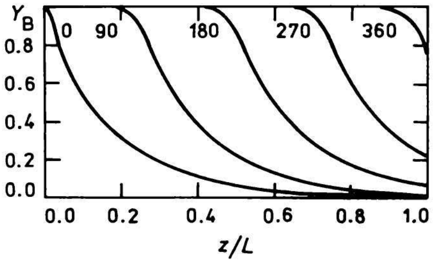


Fig. 5. Dimensionless thiophene concentration *vs.* time.
○ Experiment; ——— Model 2.



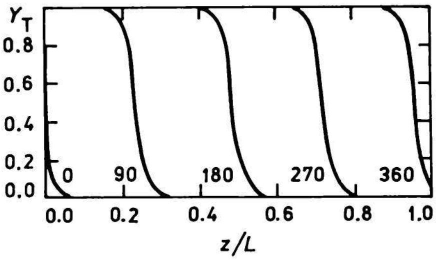


Fig. 6. Deactivation wave movement. Transient concentration Y_B profiles in the bed. Calculated results from Model 2. $G = 15$, $F = 34$; curves parametrized by t/min.

Fig. 7. Deactivation wave movement. Transient concentration Y_T profiles in the bed. Calculated results from Model 2. $G = 15$, $F = 34$, curves parametrized by t/min.

experimental and theoretical temperature profiles in the bed are in Fig. 8. With the increase of the parameter F the temperature in the reactor decreases. The values of the parameter G do not influence the steady state temperature at the start of the experiment. During the deactivation process its increase has as consequence the increase of the hot spot temperature.

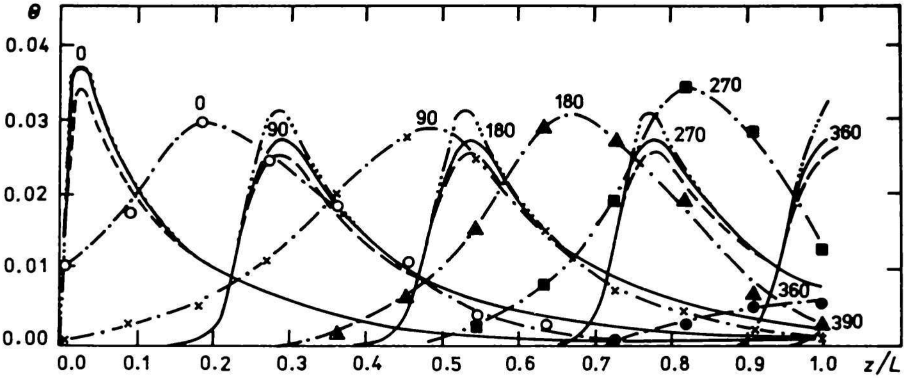


Fig. 8. Transient temperature profiles in the reactor.
Curves parametrized by t/min.
—·—·— Experiment; Model 2:
——— $G = 10, F = 34$; — — — — $G = 10, F = 36$; —···—··· $G = 15, F = 34$.

In Figs. 2 and 4 a good qualitative agreement between the model and the experiment dependences can be observed. Not so good is the agreement for thiophene (Figs. 3 and 5). It is clear that more satisfactory agreement could be obtained by a more sophisticated catalyst deactivation rate equation, which has an influence also on the slope of the benzene concentration dependence.

The thiophene concentration wave movement in the reactor is shown in Fig. 7. It indicates that the pattern of the curve and the speed of its movement, *i.e.* the deactivation wave settles down in a short time. In this paper conditions for constant speed of deactivation wave for the isothermal Model 1 are introduced. Nonisothermal conditions will be studied in a forthcoming paper.

The movement of the temperature profile (Fig. 8) indicates a good qualitative description of the process of the nonisothermal Model 2. It is clear that better agreement could be reached only by the use of a more complex model, which would involve also terms with axial or radial dispersion. Such models will be discussed in the next paper.

Symbols

A_T	dimensionless adsorbed amount	
a_L	total concentration of the active sites	mol kg^{-1}
a_T	poison adsorbed amount	mol kg^{-1}
a_{T0}	equilibrium adsorbed amount of poison, corresponding to the inlet conditions	mol kg^{-1}
C_B	concentration of the key component (benzene)	mol m^{-3}
C_{B0}	inlet concentration of the key component (benzene)	mol m^{-3}
C_H	hydrogen concentration	mol m^{-3}
C_T	thiophene concentration	mol m^{-3}
C_{T0}	inlet thiophene concentration	mol m^{-3}
c_{pg}	heat capacity of the gas	J kg^{-1} K^{-1}
c_{ps}	heat capacity of the catalyst	J kg^{-1} K^{-1}
d_t	reactor diameter	m
E	activation energy for catalytic reaction	J mol^{-1}
E_T	activation energy for deactivation	J mol^{-1}
F	dimensionless heat transfer coefficient	
$\mathcal{F}$	minimized function, see eqn *(68)*	
G	dimensionless parameter, see eqn *(13)*	
$(-\Delta H)$	heat of reaction	J mol^{-1}
h	overall heat transfer coefficient	J m^{-2} s^{-1} K^{-1}
K	adsorption constant for benzene	m^3 mol^{-1}
K_0	adsorption constant for benzene at temperature T_0	m^3 mol^{-1}
K_∞	adsorption constant for benzene at $T \rightarrow \infty$	m^3 mol^{-1}
k	reaction rate constant	m^3 kg^{-1} s^{-1}
k_∞	frequency factor of catalytic reaction	m^3 kg^{-1} s^{-1}
k_T	deactivation rate constant	m^3 mol^{-1} s^{-1}
k_{T0}	deactivation rate constant at temperature T_0	m^3 mol^{-1} s^{-1}
$k_{T\infty}$	frequency factor of deactivation	m^3 mol^{-1} s^{-1}
L	catalyst bed length	m
Q	adsorption heat of benzene	J mol^{-1}
R_s	dimensionless parameter, see eqn *(13)*	
T	temperature	K
T_0	inlet temperature	K
T_c	ambient temperature	K
t	time	s
t^0	characteristic deactivation time	s
U	dimensionless transformed time variable	
u	transformed time variable	s
V	volume of gas phase in the reactor	m^3
$\dot{V}_0$	volumetric flow rate	m^3 s^{-1}
v	deactivation wave movement velocity	m s^{-1}
W	mass of catalyst in the reactor	kg
w	velocity of fluid based upon empty cross section	m s^{-1}

X_B	conversion of key component	
Y_B	dimensionless benzene concentration	
Y_{B0}	dimensionless inlet benzene concentration	
Y_H	dimensionless hydrogen concentration	
Y_T	dimensionless thiophene concentration	
Y_{T0}	dimensionless inlet thiophene concentration	
Z	dimensionless axial coordinate	
z	axial coordinate	m
Z_L	dimensionless length of the reactor	
α_{1-4}	parameters, see eqn (*6*)	$kg\ mol^{-1}$
α_i, α_k	dimensionless parameters, see eqn (*24*)	
α_T	dimensionless parameter, see eqn (*34*)	
β	dimensionless parameter, see eqn (*24*)	
γ	parameter, see eqn (*6*)	
δ	dimensionless parameter, see eqn (*13*)	
ε	bed void fraction	
Θ	dimensionless temperature	
Θ_c	dimensionless ambient temperature	
$\varkappa_B$	dimensionless parameter, see eqn (*24*)	
$\dot{\Xi}$	dimensionless reaction rate	
$\dot{\Xi}^*$	dimensionless reaction rate at unit activity	
$\dot{\xi}_w$	reaction rate on the catalyst	$mol\ kg^{-1}\ s^{-1}$
$\dot{\xi}_w^0$	reaction rate on the fresh catalyst corresponding to the composition and the temperature of the feed	$mol\ kg^{-1}\ s^{-1}$
$\dot{\xi}_w^*$	reaction rate on the fresh catalyst	$mol\ kg^{-1}\ s^{-1}$
ϱ_b	bed density	$kg\ m^{-3}$
ϱ_g	gas density	$kg\ m^{-3}$
τ	dimensionless time	
Φ	relative activity	
$\dot{\Phi}$	deactivation rate	

References

1. Butt, J. B., in *Chemical Reaction Engineering, Advances in Chemistry Series 109,* p. 259. American Chemical Society, Washington, 1972.
2. Weng, H. S., Eigenberger, G., and Butt, J. B., *Chem. Eng. Sci. 30,* 1341 (1975).
3. Butt, J. B., Weng, H. S., and Eigenberger, G., *Chem.-Ing.-Tech. 47,* 1019 (1975).
4. Mikuš, O., Pour, V., and Hlaváček, V., *Chem. Prům. 30,* 222 (1980).
5. Hlaváček, V., *Vybrané kapitoly z reakční kinetiky I.* (Selected chapters from Reaction Kinetics I.) Státní nakladatelství technické literatury. (State Publishing House of Technical Literature.) Prague, 1971.
6. Froment, G. F., in *Chemical Reaction Engineering, Advances in Chemistry Series 109,* p. 1. American Chemical Society, Washington, 1972.

7. Hlaváček, V., *Ind. Eng. Chem. 62,* 8 (1970).
8. Rachinskii, V. V., *Vvedenie v obshchuyu teoriyu dinamiki sorbtsii i khromatografii.* Nauka, Moscow, 1964.
9. Ilavský, J. and Longauer, J., *Chem. Zvesti 32,* 145 (1978).
10. Ilavský, J., Buriánek, J., Brunovská, A., and Markoš, J., *Proc. 10th Conf. Div. Chem. Eng.*, p. 203, Šachtičky, 1982.
11. Kehoe, J. P. G. and Butt, J. B., *J. Appl. Chem. Biotechnol. 22,* 23 (1972).
12. Pexidr, V., *Chem. Prům. 22,* 56 (1972).

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